Review

Recent Advances in Microplastics Removal from Water with Special Attention Given to Photocatalytic Degradation: Review of Scientific Research

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Abstract: Microplastic pollution has become a global environmental concern with detrimental effects on ecosystems and human health. Effective removal of microplastics from water sources is crucial to mitigate their impacts. Advanced oxidative processes (AOPs) have emerged as promising strategies for the degradation and elimination of microplastics. This review provides a comprehensive overview of the application of AOPs in the removal of microplastics from water. Various AOPs, such as photocatalysis, ozonation, and Fenton-like processes, have shown significant potential for microplastic degradation. These processes generate highly reactive species, such as hydroxyl radicals, which can break down microplastics into smaller fragments or even mineralize them into harmless byproducts. The efficiency of photocatalytic oxidation depends on several factors, including the choice of photocatalysts, reaction conditions, and the physicochemical properties of microplastics. Furthermore, this review discusses the challenges associated with photocatalytic oxidation, such as the need for optimization of operating parameters and the potential formation of harmful byproducts. Overall, photocatalytic oxidation offers a promising avenue for the removal of microplastics from water, contributing to the preservation of aquatic ecosystems and safeguarding human health. However, further research is needed to address the limitations and optimize the implementation of this process for effective and sustainable microplastic remediation.

Keywords: microplastics removal; advanced oxidation processes; photocatalysis; water pollution

1. Introduction

The demand and production of plastics have experienced significant growth on a global scale. Plastics have become an integral part of modern life due to their convenience, affordability, and functional properties. The high demand for plastics is driven by several factors, including population growth, urbanization, changing lifestyles, industrial development, and technological advancements. Plastic production has increased exponentially over the years. According to industry data, global plastics production reached over 360 million metric tons in 2018 [1].

The high demand for plastics can be attributed to several key properties that make them versatile and desirable for various applications: durability, versatility, lightweight, cost-effectiveness, chemical resistance, electrical Insulation [2]. These properties, among others, contribute to the high demand for plastics in numerous industries, including packaging, construction, automotive, electronics, healthcare, and consumer goods [3], and make them an integral part of modern-day manufacturing and everyday life.

The high demand and production of plastics have led to significant environmental and sustainability challenges. Plastics are durable and resistant to degradation, leading to their accumulation in the environment, particularly in marine ecosystems. Improper waste management and plastic pollution have raised concerns about their impact on wildlife, ecosystems, and human health.

Size is the most commonly used criterion for classifying plastic waste. Particle size will be of great ecological relevance because it is an important factor that determines the interaction with biota and its fate in the environment [4]. Microplastics (MP), a subgroup of plastics with an effective diameter of less than 5 mm [5], have become an emerging micropollutant due to their widespread presence in aquatic systems and their difficulty in being recycled or removed by conventional wastewater treatment technologies [6].

MPs, which arise from the fragmentation and degradation of larger plastic materials, have gained immense importance worldwide due to their widespread presence and potential environmental and health impacts. MPs are considered contaminants of emerging concern (CEC) due to their widespread presence and potential environmental and health risks [7].

MPs can enter the environment through various pathways, including the degradation of larger plastic items, the shedding of synthetic fibers, and the release of microbeads from personal care products. Once in the environment, they can accumulate in water bodies, soil, sediments, and even in organisms. The potential risks associated with microplastics as CECs include physical harm to organisms through ingestion or entanglement, the potential for transfer through food webs, the adsorption and transport of other pollutants, and the disruption of ecological processes [8]. There are also concerns about the potential for microplastics to act as carriers for harmful chemicals and pathogens [9].

The presence of microplastics in the environment, including oceans, freshwater bodies, soil, and even the air, raises concerns due to their potential negative impacts on wildlife, ecosystems, and potentially human health. Efforts are being made to reduce the generation of microplastics, develop proper waste management strategies, and raise awareness about the issue to mitigate the environmental consequences of this form of pollution.

Particularly, the presence of MPs in water poses various risks to both aquatic ecosystems and human health. Among environmental impacts, the ingestion by marine life, including fish, shellfish, and plankton, can lead to physical blockages, reduced feeding capacity, and impaired growth and reproduction. Bioaccumulation in the tissues of organisms, as they move up the food chain, can result in higher concentrations of MPs in predators and may disrupt their physiology and behavior. MPs can settle in sediments, affecting benthic organisms and altering sediment composition [10]. This can have cascading MPs have the ability to adsorb and accumulate toxic chemicals present in water, such as persistent organic pollutants (POPs) and heavy metals. When microplastics are ingested by organisms, these chemicals can be released, potentially causing toxicological effects.

Among human concerns, MPs have been detected in drinking water sources, raising concerns about potential human exposure. The health implications of ingesting MPs through food are an active area of research, with studies focused on understanding the potential long-term effects [11].

MPs can impact the balance and functioning of aquatic ecosystems, affecting nutrient cycling, species interactions, and overall ecosystem health [12]. They also have economic implications, particularly for industries dependent on clean water resources such as fisheries, tourism, and water supply.

Microplastics in water can originate from various sources, such as fragmentation of larger plastics (bottles, bags, and packaging materials), microbeads in personal care products, synthetic fibers from textiles, and atmospheric deposition. Microplastics can also enter water bodies through atmospheric deposition. Plastic particles from sources like vehicle tire wear, industrial emissions, and plastic waste can become airborne and eventually settle on land or water surfaces, ultimately entering aquatic ecosystems.

Some industries release microplastics directly into water bodies through their manufacturing processes or improper waste disposal. These include industries involved in plastics production, recycling, textile production, and plastic-based product manufacturing. MPS can be present in wastewater discharged from domestic sources, including households, businesses, and industries. Despite wastewater treatment processes, microplastics can bypass filtration systems and enter receiving water bodies through treated effluents.

It is important to note that the sources and pathways of microplastics can vary depending on the location, local practices, and specific environmental factors. Efforts are being made to address these sources and reduce the release of microplastics into water bodies through improved waste management, regulation, and public awareness campaigns.

Several techniques have been developed to remove microplastics from water [13]. These techniques can be broadly classified into two categories: physical removal and advanced treatment methods (see Figure 1). Table 1 summarizes the advantages and disadvantages of these treatment methods, which are described in more detail below.
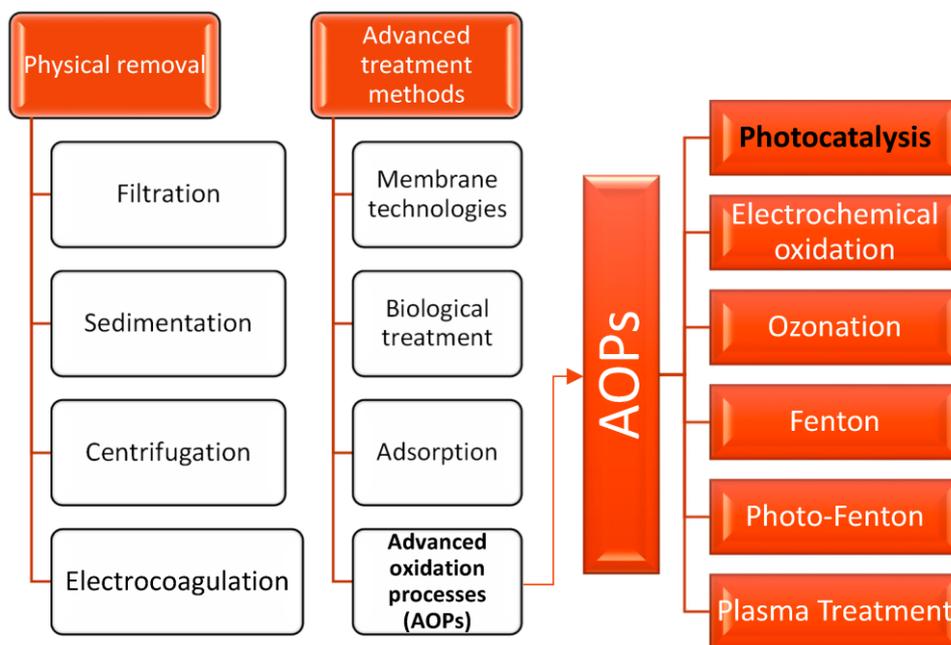

Figure 1. Classification of MP removal techniques.

Table 1. Advantages and disadvantages of physical and advanced treatment methods for MP removal.

Method Type	Method	Advantages	Disadvantages
Physical	Filtration	- Versatility - Existing infrastructure - Physical barrier	- Size limitation - Filter clogging - Limited removal of dissolved MPs - Costs and energy requirement - Disposal of capture MPs
	Sedimentation	- Cost-effective - Simple operation - High removal efficiency	- Inefficient for small particles - Time-consuming - Space requirement - Continuous maintenance
	Centrifugation	- High Removal - Rapid Process - Versatility - Scalability	- Energy Consumption - Limited Efficiency for Small Particles - Equipment and Maintenance - Potential Damage to Fragile Samples

Table 1. *Cont.*

Method Type	Method	Advantages	Disadvantages
Advanced	Electrocoagulation	- Effective Removal Efficiency - Wide Applicability - Potential for Simultaneous Pollutant Removal - Scalability - Lower Chemical Usage	- Energy Consumption - Equipment and Maintenance - Limited Removal Efficiency for Small Particles - Electrode Fouling
	Membrane technology	- High Removal Efficiency - Versatility - Scalability - Continuous Operation - Additional Pollutant Removal	- Fouling - Energy Requirements - Membrane Lifespan and Maintenance - Cost
	Biological treatment	- Environmentally Friendly - Potential for Complete Degradation - Cost-Effective - Potential for Synergistic Effects	- Limited Efficiency for Certain Types of Microplastics - Slow Treatment Rate - Biological Interference - Challenges in Monitoring and Control
	Adsorption	- High Removal Efficiency - Versatility - Additional Pollutant Removal - Potential for Regeneration	- Limited Adsorption Capacity - Specificity - Cost - Disposal of Used Adsorbents
Advanced	AOPs	- High Efficiency - Versatility - Wide Range of Applicability - Degradation of Persistent and Hazardous Substances - Chemical-Free or Low-Chemical Consumption Options - Potential for Scale-up - Synergy with Other Treatment Processes	- Cost considerations - Energy requirements - The need for careful optimization to ensure optimal performance

The aim of this literature review is to summarize the main characteristics of the methods used for the removal of MPs from water, as well as their main advantages and disadvantages. In particular, the last reported results on the photoelectrochemical removal of MPs and the main parameters affecting the performance of the described photocatalysts are discussed.

2. Physical and Advanced Methods

2.1. Physical Methods

Physical methods for microplastics removal refer to techniques or processes that involve physically separating or extracting microplastic particles from various environments. These methods typically rely on physical characteristics such as size, density, and behavior of microplastics to facilitate their removal.

2.1.1. Filtration

Filtration involves passing water through a filter medium that can physically trap and remove microplastic particles. Various types of filters, such as mesh screens, sieves, and membranes, can be used for this purpose. Filtration can be highly effective in removing microplastics from water. It can capture particles of various sizes, including the smaller microplastics that might otherwise be challenging to remove through other methods.

Filtration methods have demonstrated promising outcomes in eliminating microplastics from water. In-line filtration, in particular, has proven to be more efficient in recovering microplastics and holds greater potential for reducing microplastic contamination compared to in-lab filtration [14].

Combining electrocoagulation–electroflotation (EC/EF) with membrane filtration has also shown effectiveness in purging microplastics from wastewater, achieving maximum removal efficiencies of 100% [15].

- Advantages:
  - Versatility since it can be applied to various water sources, including wastewater treatment plants and drinking water treatment systems, and it can be adapted and customized to suit different scales and requirements;
  - Existing Infrastructure: Filtration can be integrated into existing water treatment infrastructure, making it a feasible option for retrofitting or upgrading existing systems to address microplastic contamination;
  - Physical Barrier: Filtration provides a physical barrier that can efficiently separate microplastics from water without the need for chemical additives or complex processes. This simplicity can make it a cost-effective and reliable method.

- Disadvantages:
  - Size Limitations: While filtration can capture a wide range of microplastics, the efficiency may vary depending on the size of the particles. Extremely small microplastics or nanoplastics may pass through certain filters, requiring additional treatment or the use of specialized filter media;
  - Filter Clogging: continuous filtration of water containing high concentrations of microplastics can lead to clogging of filters. Regular maintenance and cleaning of filters may be necessary to ensure optimal performance and prevent system disruptions;
  - Limited Removal of Dissolved Microplastics: Filtration is primarily effective in removing larger microplastic particles, but it may not be as efficient in removing dissolved microplastics or nanoplastics, which are microscopic in size and dispersed within the water,
  - Cost and Energy Requirements: Filtration systems, especially those designed to handle large volumes of water, can require significant initial investment and ongoing operational costs. Additionally, the energy required to maintain the flow rate through the filters should be considered. Disposal of Captured Microplastics: Proper disposal of the captured microplastics from the filters is a challenge. The collected microplastics may need to be managed and disposed of appropriately to prevent their re-entry into the environment.

2.1.2. Sedimentation

Sedimentation techniques allow microplastics to settle at the bottom of a container or water body. This method relies on the density difference between microplastics and water. Coagulants or flocculants may be added to enhance the settling process.

Several research papers have investigated the removal of microplastics from water through sedimentation. Shen et al. [16] conducted a study using electrocoagulation (EC) with an aluminum anode and found it to be effective in removing microplastics from wastewater. In all their experiments, they achieved removal rates above 80%. Elkhatib et al. [17] also explored electrocoagulation methods and reported that microplastic removal efficiency reached at least 99% when using synthetic solutions with specific pH values and current densities. Akarsu et al. [14] focused on the electrocoagulation–electroflotation (EC/EF) process and membrane filtration for microplastic removal, achieving maximum removal efficiencies of 100% for various polymer types. Xue et al. [18] delved into the removal of carboxylated polystyrene microspheres in drinking water treatment processes and observed that higher alum doses generally resulted in better removal of microspheres smaller than 90 μm. Lastly, Lee and Jung [19] investigated the coagulation method for removing seawater microplastics, and they achieved high removal efficiencies exceeding 60% using various coagulants.

- Advantages:

Cost-Effective: Sedimentation is a relatively low-cost method as it does not require complex equipment or extensive energy consumption [20].

Simple Operation: It is a straightforward process that does not require advanced technical expertise to operate. It can be easily implemented in various settings. Sedimentation can be used not only in primary treatment but also in secondary treatment [21].

High Removal Efficiency: Sedimentation can achieve a relatively high removal efficiency for larger microplastic particles that settle quickly under gravity.

- Disadvantages:

Inefficient for Small Particles: Sedimentation is less effective for smaller microplastic particles that take longer to settle due to their lower density. These particles may remain suspended in the water and not settle adequately [21].

Time-Consuming: The sedimentation process can be time-consuming as it requires a significant amount of time for the microplastics to settle completely, especially for smaller particles.

Space Requirement: Sedimentation tanks or settling basins require sufficient space for the water to be held and for the microplastics to settle. This may pose a challenge in limited space or densely populated areas.

Continuous Maintenance: Regular cleaning and maintenance of sedimentation tanks are necessary to remove accumulated settled microplastics and prevent clogging.

2.1.3. Centrifugation

Centrifugation involves spinning water at high speeds to separate microplastics by their density. The centrifugal force causes the microplastics to move towards the outer edge, facilitating their removal [22].

Murray et al. [23] investigated the impact of centrifugation on the removal of nanoplastics using various centrifuge times and speeds. The primary objective was to assess the potential escape of nanoplastics during wastewater treatment, particularly in biosolids dewatering, where they might re-enter the wastewater influent. It was observed that the percent removal substantially increased as the centrifuge speed rose from 5000 to 7000 rpm, escalating from $49 \pm 10\%$ to $80 \pm 7\%$. The increase in removal was more gradual between 8000 and 10,000 rpm, where it reached $84 \pm 4\%$ to $94 \pm 6\%$. On the other hand, the percent removal showed a sharp increase as the centrifuge time increased from 0 to 3 min, rising from $36 \pm 7\%$ after 1 min to $94 \pm 6\%$ after 3 min. The rate of increase in percent removal became more gradual for longer centrifuge times, eventually reaching $99 \pm 1\%$ for a 10 min centrifuge time.

Continuous flow centrifugation has been proposed as an alternative technique for sampling microplastic from water bodies. This technique offers advantages such as volume reduction, efficient removal of microplastic from suspensions, and no change in particle size distribution [24]. Additionally, the use of continuous flow centrifugation has been shown to enable size- and density-selective sampling of microplastic particles [25].

- Advantages:

High Removal Efficiency: Centrifugation can achieve a high removal efficiency for microplastics, especially for larger particles, as they can be separated and collected through the centrifugal force generated by the high-speed rotation.

Rapid Process: Centrifugation is generally a fast process, allowing for efficient separation and collection of microplastics within a relatively short period.

Versatility: Centrifugation can be applied to various types of water samples, including both freshwater and wastewater, making it a versatile method for microplastic removal.

Scalability: The centrifugation process can be easily scaled up or down depending on the volume of water to be treated, making it suitable for both small-scale and large-scale applications.

- Disadvantages:

Energy Consumption: Centrifugation requires significant energy input to generate the high-speed rotation needed for effective separation. This can result in higher operational costs and environmental impacts.

Limited Efficiency for Small Particles: Centrifugation may be less efficient for smaller microplastic particles that have a lower settling velocity. These particles may not be effectively separated and collected by centrifugal force, leading to incomplete removal.

Equipment and Maintenance: Centrifuges are specialized equipment that can be costly to purchase, operate, and maintain. Regular maintenance and calibration are necessary to ensure optimal performance.

Potential Damage to Fragile Samples: Some microplastic samples, such as microfibers, can be fragile and easily damaged by high centrifugal forces. Care must be taken to avoid sample degradation during the centrifugation process.

2.1.4. Electrocoagulation

This method utilizes an electric current to destabilize and agglomerate microplastic particles. The agglomerated microplastics can then be easily removed through processes like sedimentation or filtration [26,27].

Numerous investigations have explored the effectiveness of electrocoagulation (EC) in eliminating microplastics and have identified key factors that contribute to high removal rates. Notably, the use of aluminum anodes has proven more efficient than iron anodes in the removal of microplastics [16]. Moreover, achieving a pH of 7.2 can lead to a removal efficiency of more than 90% [17], while the removal of fiber microplastics outperforms that of granular microplastics [14].

To further enhance the removal efficiency of microplastics, researchers have found that increasing the concentration of the electrolyte and applying higher voltage density are effective measures [28]. The optimal conditions for EC, as supported by the research, involve an electrolyte concentration of 0.05 M, pH of 7.2, 10 V of applied voltage density, and utilization of aluminum anodes [29].

- Advantages:

Effective Removal Efficiency: Electrocoagulation has shown promising results in removing microplastics from water, achieving high removal efficiencies. The coagulating agents formed during the process can effectively bind to microplastics, facilitating their separation.

Wide Applicability: Electrocoagulation can be applied to various types of water sources, including freshwater and wastewater. It can be effective in treating different concentrations and types of microplastics, making it a versatile method.

Potential for Simultaneous Pollutant Removal: Electrocoagulation can also help remove other pollutants present in the water, such as organic compounds, heavy metals, and suspended solids. This makes it a potentially comprehensive solution for water treatment.

Scalability: Electrocoagulation systems can be scaled up or down to accommodate different volumes of water, making them suitable for both small-scale and large-scale applications.

Lower Chemical Usage: Electrocoagulation typically requires fewer chemicals compared to traditional coagulation methods, reducing the need for chemical additives and associated costs.

- Disadvantages:

Energy Consumption: Electrocoagulation requires electricity to generate the coagulating agents and facilitate the separation of microplastics. This can result in higher energy consumption and associated costs.

Equipment and Maintenance: Electrocoagulation systems can be complex and require specialized equipment for the application of electric currents. Proper maintenance, monitoring, and calibration of the equipment are necessary for optimal performance.

Limited Removal Efficiency for Small Particles: Electrocoagulation may be less efficient in removing smaller microplastic particles due to their lower settling velocity. Additional post-treatment steps may be required to achieve the complete removal of smaller particles.

Electrode Fouling: During the electrocoagulation process, the electrodes can become fouled or coated with reaction byproducts, reducing their effectiveness. Regular cleaning and maintenance are required to prevent electrode fouling and ensure consistent performance.

2.2. Advanced Treatment Methods

2.2.1. Membrane Technologies

Advanced membrane filtration techniques, such as ultrafiltration and nanofiltration, are effective in removing microplastics. These membranes have specific pore sizes that can selectively exclude microplastics while allowing water to pass through [30].

Membrane technologies have exhibited promising outcomes in effectively eliminating microplastics (MPs) from wastewater. A notable example is the electrocoagulation–electroflotation (EC/EF) process, which achieved a remarkable 100% removal efficiency for two different polymer types by utilizing various electrode combinations, pH levels, and reaction times [31]. Similarly, membrane filtration demonstrated exceptional efficacy with 100% removal efficiency for MPs as well [14].

Moreover, the fertilizer-driven forward osmosis (FDFO) process, implemented through a membrane system, proved highly successful in completely removing both MPs and nanoplastics (NPs) from wastewater, resulting in the production of high-quality irrigation water [32]. Additionally, the FDFO process effectively mitigated membrane fouling attributed to extracellular substances [33].

Furthermore, the air flotation and nano-ferrofluid processes also displayed commendable removal efficiency for MPs and NPs, and when coupled with membrane techniques like ultrafiltration and microfiltration, these processes successfully eliminated over 90% of fragment particles [34].

In summary, membrane technologies, encompassing EC/EF, membrane filtration, FDFO, air flotation, and nano-ferrofluid processes, have consistently showcased excellent results in the removal of microplastics from wastewater.

- Advantages:

High Removal Efficiency: Membrane technologies can achieve high removal efficiencies for microplastics, including both large and small particles. The microporous or semi-permeable membranes act as physical barriers, effectively filtering out microplastics from water.

Versatility: Membrane technologies can be applied to various water sources, including freshwater, wastewater, and seawater. They can remove a wide range of microplastics, including both floating and suspended particles.

Scalability: Membrane systems can be easily scaled up or down to accommodate different volumes of water, making them suitable for both small-scale and large-scale applications.

Continuous Operation: Membrane filtration can operate continuously, allowing for consistent removal of microplastics over time. It can be integrated into existing water treatment systems or used as a standalone unit.

Additional Pollutant Removal: Membrane technologies can also remove other contaminants present in the water, including suspended solids, bacteria, and certain dissolved substances. This provides an added benefit for overall water quality improvement.

- Disadvantages:

Fouling: Membranes can become fouled over time, especially in the presence of high concentrations of suspended solids or organic matter. Fouling reduces the efficiency of microplastic removal and requires regular cleaning or replacement of membranes.

Energy Requirements: Membrane filtration processes typically require energy to maintain the pressure needed for water to pass through the membranes. The energy consumption can vary depending on the type of membrane technology used and the operating conditions.

Membrane Lifespan and Maintenance: Membranes have a limited lifespan and may require periodic replacement or maintenance to ensure optimal performance. This adds to the operational and maintenance costs of the membrane system.

Cost: The initial installation and operational costs of membrane systems can be relatively high, especially for advanced membrane technologies like reverse osmosis. Cost considerations should be taken into account when selecting the appropriate membrane technology for microplastic removal.

2.2.2. Biological Treatment

Some microorganisms have the ability to degrade or assimilate microplastics. Biological treatment methods, such as bioreactors or biofilters, utilize these microorganisms to remove microplastics from water [35].

Various biological methods are employed for the degradation of microplastic contaminants, involving a range of organisms such as algae, fungi, bacteria, enzymes, zooplankton, sea clams, corals, and marine microorganisms like archaeans and eukaryotes. Additionally, bio-polymers like lignin, cellulose, chitin, and starch play a role in eliminating microplastics by forming larger flocs, which can be subsequently removed [36]. Out of these approaches, some particularly effective methods for plastic degradation include adsorption by seaweed microalgae, specifically Fucus vesiculosus, the use of modified starch biopolymers, ingestion by marine organisms like Red Sea giant clams, and the involvement of marine fungus, Zalerion maritimum.

- Advantages:

Environmentally Friendly: Biological treatment methods are considered environmentally friendly as they utilize natural processes and organisms to degrade or remove microplastics. They do not involve the use of chemicals or produce harmful byproducts.

Potential for Complete Degradation: Biological treatment methods have the potential to completely degrade microplastics, converting them into non-harmful substances such as water, carbon dioxide, and biomass. This can contribute to the overall remediation of microplastic pollution.

Cost-Effective: Biological treatment methods can be cost-effective compared to other treatment technologies as they do not require extensive infrastructure or high-energy consumption. They utilize natural processes and can be implemented in various settings, including wastewater treatment plants and natural water bodies.

Potential for Synergistic Effects: Biological treatment methods can have synergistic effects by simultaneously targeting other organic pollutants present in the water, thereby providing a comprehensive water treatment solution.

- Disadvantages:

Limited Efficiency for Certain Types of Microplastics: Biological treatment methods may have limited efficiency for certain types of microplastics, particularly those with low biodegradability or resistance to biological degradation. Certain microplastic polymers, such as polyethylene and polypropylene, may require more time and specialized conditions for effective degradation.

Slow Treatment Rate: Biological treatment methods can be relatively slow compared to other physical or chemical treatment methods. The time required for complete microplastic degradation or removal can vary depending on factors such as microplastic type, size, and environmental conditions.

Biological Interference: Biological treatment methods can be affected by the presence of other organic matter, chemicals, or substances in the water that may interfere with

the activity of microorganisms responsible for microplastic degradation. Water quality parameters need to be carefully managed to optimize the biological treatment process.

Challenges in Monitoring and Control: Monitoring and controlling the biological treatment process can be challenging due to the complex interactions between microorganisms, microplastics, and environmental conditions. Close monitoring and control measures are required to ensure consistent and efficient microplastic removal.

2.2.3. Adsorption

Adsorption techniques use materials with a high affinity for microplastics, such as activated carbon or specialized resins. These materials can adsorb microplastics onto their surfaces, allowing for their removal from the water [37].

Adsorption can be categorized into two types: physical adsorption and chemical adsorption [38–40]. Physical adsorption involves the interaction of intermolecular forces, such as Van der Waals forces, while chemical adsorption is based on chemical bonding, like covalent bonding, ionic bonding, and hydrogen bonding [41]. Physical adsorption typically occurs at low temperatures, exhibiting rapid adsorption rates, low heat of adsorption, and non-selective adsorption. Conversely, chemical adsorption is a process that involves the formation and breaking of chemical bonds, requiring higher temperatures and displaying selectivity [42].

Researchers have successfully developed novel composite materials for effectively adsorbing microplastics (MPs). These composites fall into two categories: powder composites [39,40] and sponge composites [43,44]. Each category follows a different process for adsorbing MPs. Powder composite materials typically require mixing with MPs first and then separation using various physical methods, such as high-speed centrifugation or magnetic extraction. For example, one successful eco-friendly adsorbent was synthesized by modifying fly ash (FA) with iron ions to remove polystyrene MPs [43]. The adsorption process involved adding the adsorbent to an MP suspension, mixing, and then separating through high-speed centrifugation. Extensive characterizations demonstrated strong interactions between the iron-modified FA and MPs, with adsorption mechanisms mainly driven by electrostatic attraction, complexation, and π–π interactions. The magnetic adsorption material exhibited an impressive adsorption capacity for MPs (82.8 to 89.9 mg/g) at pH levels between 5 and 7.

- Advantages:

High Removal Efficiency: adsorption can achieve high removal efficiencies for microplastics, including both large and small particles. The adsorbent material has a high affinity for microplastics, effectively capturing and removing them from the water.

Versatility: Adsorption can be applied to various water sources and microplastic types. Different adsorbent materials can be used, such as activated carbon, zeolites, and specific polymers, allowing for customization based on the specific requirements of the water treatment process.

Additional Pollutant Removal: Adsorbent materials used for microplastic removal can also adsorb and remove other pollutants present in the water, such as organic compounds, heavy metals, and certain chemicals. This provides an added benefit for overall water quality improvement.

Potential for Regeneration: In some cases, adsorbent materials can be regenerated and reused, which can reduce the overall operational costs and environmental impact associated with the disposal of used adsorbents.

- Disadvantages:

Limited Adsorption Capacity: The adsorption capacity of the adsorbent material is finite, and once it reaches its saturation point, it may need to be replaced or regenerated. This can increase the operational and maintenance costs of the adsorption process.

Specificity: Adsorption can be selective, meaning that certain types of microplastics may have a higher affinity for certain adsorbents. It may be necessary to use a combination

of adsorbent materials or conduct pre-treatment processes to enhance the efficiency of microplastic removal.

Cost: The cost of adsorbent materials can vary, and certain adsorbents may be more expensive than others. This can impact the overall cost-effectiveness of the adsorption process.

Disposal of Used Adsorbents: Disposal of used adsorbents, particularly if they contain captured microplastics, needs to be considered. Proper disposal methods should be implemented to prevent any potential environmental contamination.

2.2.4. Advanced Oxidation Processes (AOPs)

AOPs involve the use of powerful oxidizing agents or radiation to break down microplastics. Examples include ozonation, photocatalysis, and advanced oxidation with hydrogen peroxide.

It is important to note that the effectiveness of these techniques can vary depending on factors like the type and size of microplastics, water quality parameters, and the specific implementation of the method. A combination of multiple techniques may be required to achieve optimal removal efficiency. Ongoing research and development are focused on improving these techniques and exploring innovative approaches to address the challenge of microplastic pollution in water.

Particularly, advanced oxidative processes (AOPs) offer several advantages in the removal of microplastics from water, such as:

High Efficiency: AOPs are known for their high removal efficiency when it comes to microplastics. These processes can effectively break down and degrade microplastic particles, resulting in their removal from the water. AOPs can achieve removal rates of varying degrees, depending on the specific technique and operational conditions employed.

Versatility: AOPs are versatile and can be applied to different water sources and treatment scenarios. They can be used in the treatment of both freshwater and wastewater, making them applicable to various industries and settings.

Wide Range of Applicability: AOPs are effective against a broad spectrum of microplastics, including different types of polymers and varying particle sizes. They can target both primary microplastics (e.g., microbeads) and secondary microplastics resulting from the fragmentation of larger plastic debris.

Degradation of Persistent and Hazardous Substances: AOPs not only remove microplastics but also have the potential to degrade and break down persistent organic pollutants (POPs) and other hazardous substances that may be adsorbed or associated with microplastic particles. This helps in addressing the issue of chemical contamination associated with microplastics in water.

Chemical-Free or Low-Chemical Consumption Options: Some AOPs, such as photocatalysis using UV light and advanced oxidation with hydrogen peroxide, can be implemented without the addition of harmful chemicals or with low chemical consumption. This makes them relatively environmentally friendly compared to other chemical-based treatment methods.

Potential for Scale-up: AOPs can be scaled up to treat larger volumes of water, making them suitable for industrial applications and municipal water treatment facilities.

Synergy with Other Treatment Processes: AOPs can complement and enhance other water treatment processes. They can be combined with physical removal techniques like filtration or sedimentation to achieve a comprehensive microplastic removal strategy.

Despite these advantages, it is important to note that AOPs also have limitations, such as cost considerations, energy requirements, and the need for careful optimization to ensure optimal performance. Additionally, the specific AOP technique employed and the water quality parameters can influence the efficiency and effectiveness of microplastic removal. Ongoing research and development are focused on improving the performance and cost-effectiveness of AOPs for microplastic removal in water treatment.

Among the AOPs that have been used or explored for the removal of microplastics in water:

- Photocatalysis

Photocatalysis involves the use of a photocatalyst, typically titanium dioxide (TiO_2), activated by ultraviolet (UV) light. When the photocatalyst is exposed to light, it generates reactive oxygen species (ROS) that can degrade microplastic particles. This process has shown promise in laboratory studies and pilot-scale applications.

- Electrochemical Oxidation

Electrochemical oxidation utilizes an electric current to induce chemical reactions that lead to the degradation of microplastics. It involves the application of an electric potential between two electrodes in the presence of water and microplastics, leading to the generation of ROS and the subsequent breakdown of microplastic particles.

At present, electrochemical methods for the identification and removal of microplastics and nanoparticles (MP/NP) are in their early stages of development. This field faces several challenges and holds promising prospects. Some of the key areas of focus are the advancement of electrochemical devices and electrodes, the effective treatment of real-world urban waters, the integration of techniques to achieve high removal performance, and the exploration of electrochemical upcycling processes for MP/NP [45].

In essence, the field of electrochemical MP/NP identification and removal is still evolving, with ongoing efforts directed toward overcoming challenges and harnessing its potential for practical applications in environmental remediation and resource recovery.

Ozonation: Ozone (O_3) is a powerful oxidizing agent that can be used to degrade microplastics. Ozonation involves the introduction of ozone gas into water, where it reacts with microplastics, leading to their degradation and eventual removal. This process has been explored for the treatment of microplastics in both laboratory and pilot-scale studies.

- Fenton and Photo-Fenton Processes

The Fenton process involves the reaction between hydrogen peroxide (H_2O_2) and iron salts in the presence of an acid, generating hydroxyl radicals ($\bullet OH$) that can degrade microplastics. The Photo-Fenton process combines the Fenton process with UV light, enhancing the generation of hydroxyl radicals and degradation efficiency.

Previous studies have shown that the Fenton process is ineffective in degrading polystyrene (PS) materials. However, Feng et al. [46] explored the decomposition of PS microspheres using the photo-assisted Fenton process, but other studies on polystyrene photodegradation primarily focused on large plastic films rather than MPs or nanoparticles [47,48]. The availability of oxidants is a crucial limiting factor in Fenton-based reactions. Furthermore, the release of iron ions and the formation of significant amounts of sludge pose challenges to the practical application due to the scavenging effect of H_2O_2 on free radicals [49,50]. Recognizing these limitations, Kang et al. [6] investigated the decomposition of cosmetic MPs using catalytic activation of peroxymonosulfate to generate active radicals based on robust carbon nanosprings. Although this advanced oxidation process was unable to directly convert cosmetic MPs into value-added products, microorganisms could potentially digest the non-toxic organic by-products generated during MPs degradation and transform them into useful substances like proteins, biofuels, and sugars. This approach aligns with environmentally friendly and sustainable practices and enables the carbon cycle in nature. Building upon these findings, the following section will discuss the photocatalytic degradation of MPs on catalysts.

- Plasma Treatment

Plasma treatment involves subjecting the water containing microplastics to a plasma discharge. The plasma generates reactive species that can chemically degrade the microplastic particles. This technique has shown promise in laboratory-scale experiments for the removal of microplastics.

Ongoing research in this field indicates that plasma-based methods have significant potential to tackle the escalating issue of microplastic pollution in water bodies, thereby contributing to the improvement of water quality and environmental health.

It is important to note that several studies have investigated the application of AOPs for microplastic removal, and they often discuss the efficiency and parameters affecting the removal for each technique used.

Particularly, photocatalysis provides several advantages over other advanced oxidation processes (AOPs) for microplastic removal from water. Some of these advantages include environmental friendliness. Photocatalytic degradation is based on the activation of catalysts through light energy, typically from natural sources like sunlight. This process does not require the use of additional chemicals or reagents, reducing the potential for secondary pollution and minimizing environmental impact. Selectivity: Photocatalytic degradation can be selectively targeted towards specific contaminants, such as microplastics, while leaving other components of the water intact. This selectivity helps minimize potential unwanted consequences and allows for more precise treatment of contaminated water. Wide applicability: Photocatalytic degradation can be applied to a wide range of microplastics, regardless of their chemical composition or size. This versatility makes it suitable for treating different types of microplastics found in various water sources. Efficiency: Photocatalytic degradation processes can achieve high degradation rates and efficient removal of microplastics under optimal conditions. The use of catalysts improves reaction kinetics and accelerates the breakdown of microplastic particles, leading to effective removal. Regeneration potential: Catalysts used in photocatalytic degradation can be regenerated and reused, making the process cost-effective and sustainable in the long term. This reduces the need for constant replacement of catalysts and lowers operational costs. Scalability: Photocatalytic degradation processes can be easily scaled up to treat large volumes of water, making them suitable for industrial applications and water treatment plants. Overall, the advantages of photocatalytic degradation make it a promising approach for the removal of microplastics from water, offering an efficient, environmentally friendly, and versatile solution to address this serious pollution problem. This review focuses on the analysis of the reported results, gathering the main findings. Thus, this work provides valuable insights into the effectiveness of photocatalytic removal and the factors that influence their performance in removing MPs.

3. A Review of Photocatalytic Systems: Exploring Catalysts, Reactive Species, and Influencing Factors in MP Degradation

Photocatalysis involves the use of a catalyst, typically a semiconductor material, to accelerate a chemical reaction in the presence of light. For MP degradation, the photocatalyst is typically employed to generate reactive oxygen species (ROS) upon exposure to light. These ROS, such as hydroxyl radicals (OH·), possess high reactivity and can break down the chemical bonds in microplastics, leading to their degradation. Titanium dioxide (TiO_2) and zinc oxide (ZnO) are the most commonly used photocatalysts in microplastic degradation studies. Both semiconductors have an appropriate bandgap, 3.2 eV for TiO_2 and 3.4 eV for ZnO [51], which, upon light interaction, leads to the generation of various reactive species. When semiconductors are excited by light with energy higher than the bandgap, charge separation occurs, resulting in the release of free electrons that transition from the valence band to the conduction band. Several significant reactive species are formed during the interaction with light. Consequently, photoexcitation creates a "hole" in the valence band of the semiconductor. When photocatalysts are illuminated with ultraviolet (UV) light, they can generate ROS, which reacts with the microplastic surface and initiate degradation processes.

It has been reported that several factors affect the photocatalytic degradation of MPs [52], including the properties of the MPs (structure, size, and shape), the materials used for the formation of the photocatalyst (doping element and content), and primarily

environmental factors such as humidity, temperature, light intensity, and wavelength. Table 2 provides selected results of the use of photocatalysis for the MPs removal.
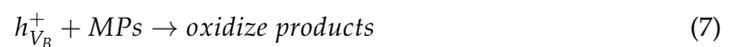
Titanium dioxide (TiO_2) is a well-known photocatalyst with significant photocatalytic activity. Its photocatalytic properties are primarily attributed to its wide bandgap energy, high chemical stability, non-toxicity, and abundance. When exposed to ultraviolet (UV) light, TiO_2 can initiate a series of photochemical reactions due to its ability to generate electron-hole pairs.

The photocatalytic reaction initiates when light irradiation promotes the electron from the VB to the vacant CB. The incident photon possesses energy equal to or greater than the bandgap of TiO_2. This excitation results in the generation of holes (h^+) in the VB. The overall reaction under light irradiation can be summarized by Equation (1) [53]. When a hole in the VB encounters a water molecule, it undergoes a reaction that yields hydroxyl radicals ($\bullet OH$), as shown in Equation (2). The hydroxyl radical ($\bullet OH$) is a potent oxidizing agent and holds significant importance in photooxidation processes [54,55].

$$TiO_2 \xrightarrow{h\nu} h^+_{V_B} + e^-_{C_B} \tag{1}$$

$$h^+_{V_B} + H_2O \rightarrow \bullet OH + H^+ \tag{2}$$

$$O_2 + e^-_{C_B} \rightarrow O_2^{\bullet -} \tag{3}$$

$$O_2^{\bullet -} + H^+ \rightarrow HOO^\bullet \tag{4}$$

$$2HOO^\bullet \rightarrow O_2 + H_2O_2 \tag{5}$$

$$H_2O_2 \rightarrow 2OH^\bullet \tag{6}$$

The hydroxyl radical *($\bullet OH$)* generated by the photocatalyst exhibits non-selective reactivity towards adsorbed contaminants that are attached or in close proximity to the surface of the photocatalyst. This reactivity results in the mineralization of the contaminants. TiO_2 is particularly effective in the photodegradation of organic pollutants, both under UV and visible light irradiation.

The photoexcited electron in the CB engages in a reaction with an oxygen molecule, resulting in the formation of superoxide radicals ($O_2^{\bullet -}$) as described by Equation (3). These $O_2^{\bullet -}$ radicals actively participate in oxidation reactions while also preventing the recombination of photogenerated electron-hole pairs. This process helps maintain the electron neutrality within the semiconductor [56]. The generated $O_2^{\bullet -}$ radical undergoes protonation to form hydroperoxyl radical ($HO_2\bullet$), as depicted in Equation (4). The hydroperoxyl radical ($HO_2\bullet$) then reacts to produce hydrogen peroxide (H_2O_2) according to Equation (5). Subsequently, H_2O_2 dissociates to yield $\bullet OH$ radicals, as shown in Equation (6). To facilitate comprehension, the overall reaction to plastic degradation is illustrated through the following Equations (7)–(9).

$$h^+_{V_B} + MPs \rightarrow oxidize\ products \tag{7}$$

$$\bullet OH + MPs \rightarrow CO_2 + H_2O \tag{8}$$

$$e^- + MPs \rightarrow reduced\ products \tag{9}$$

Under visible light, there is also a certain degree of direct degradation of MPs by TiO_2. This process involves the excitation of MPs from their ground state to an excited state upon the incidence of visible light photons. In this excited state, the plastics generate semi-oxidized cation radicals through the injection of electrons into the CB of the catalyst. The trapped electrons then react with dissolved oxygen, resulting in the formation of $O_2^{\bullet -}$. These $O_2^{\bullet -}$ radicals subsequently give rise to $\bullet OH$ radicals, which are responsible for the decomposition of the target pollutants. The indirect mechanism of plastic degradation prevails over the direct mechanism, with plastic decomposition being more prominent than the reaction induced by visible light. Furthermore, the reactions initiated by visible light are considerably slower compared to those triggered by UV light.

The $OH\bullet$ and $O_2^{\bullet-}$ radicals produced additionally initiate degradation at vulnerable points along the long polymeric chains of low-density polyethylene (LDPE), resulting in the formation of low molecular weight polyethylene alkyl radicals $((-CH_2-CH\bullet-)n)$. Moreover, it has been demonstrated that the photogenerated hole (h^+) can react with organic compounds, leading to the formation of organic free radicals [57].

On the other hand, Photodegradation (in the absence of a catalyst) plays a crucial role in the breakdown of polymers [58]. When it comes to microplastics (MPs), prolonged exposure to sunlight, particularly UV light, can lead to the generation of environmentally free radicals, oxygen addition, hydrogen abstraction, and the breaking or linking of chemical chains [59]. This process can also result in morphological changes such as flaking and cracking [60], with UV light being identified as the primary influencing factor. However, the natural photodegradation of MPs is difficult to control. Song et al. [61] have observed the formation of oxygen-containing groups and cracks on the surfaces of MPs during laboratory-accelerated photodegradation. Nevertheless, there is limited information on the impact of reactive oxygen species (ROS) on the aging process of MPs due to their relatively low concentration in aquatic environments. Moreover, the photodecomposition of MPs is slow in the wild, especially in aquatic locations. Zhu et al. [62] investigated the aging of PS as a model in an aquatic environment under simulated sunlight for up to 150 days. They discovered the presence of ROS in the PS suspension due to light exposure. The study shed light on the mechanism of ROS formation and photodegradation of MPs under simulated sunlight. However, the study did not examine the extent of photoaging or the types of intermediate products in this photochemical system. Additionally, long-term exposure to simulated light irradiation can lead to excessive energy consumption or even light pollution.

Table 2. Selected results of the photocatalytic removal of MPs by bare and modified TiO_2.

Photocatalysts	MPs	Conditions		Degradation Efficiency (%)		Ref.
TiO_2	LDPE film	- TiO_2 (450 °C) - +UV-A, 9 days		-	4.94 WL	[57]
		- TiO2 (900 °C) - +UV-A, 9 days		-	3.98 WL	
		- TiO2 (450 °C) - +UV-C, 9 days		-	9.25 WL	
		- TiO2 (900 °C) - +UV-C, 9 days		-	17.30 WL	
	PS	400 nm-PS UV-light 12 h 254 nm Solid phase	TXT-TiO_2	-	98.40 [WL]	
			ET-TiO_2	-	91.04 [WL]	
			WT-TiO_2	-	69.25 [WL]	
TiO_2		UV-light 24 h 254 nm TXT-TiO_2	700 nm	-	93.49 [WL]	[63]
			1000 nm	-	95.30 [WL]	
			5000 nm Solid phase	-	99.00 [WL]	
			5000 nmLiquid phase	-	44.66 [WL]	

Table 2. *Cont.*

Photocatalysts	MPs	Conditions		Degradation Efficiency (%)	Ref.
		UV-light, 254 nm, 36 h TXT-TiO$_2$		- 100 WL	
				- 56 WL	
Ag/TiO$_2$		Particle size: 100–150 nm 4 h under UV irradiation		- 68 WL	[64]
Ag/TiO$_2$-RGO	PE			- 76 WL	
			- 100–125 mm	- 100 WL	
Ag/TiO$_2$		- UV radiation - 2 h, 2000 rpm	- 125–150 mm	- 100 WL	[65]
			- 150–250 mm	- 100 WL	
N-doped TiO$_2$	PET	- 300 W Xe lamp, AM 1.5 radiation		- 29 WL	[66]

WL: degradation efficiency estimated by weight losing.

3.1. Bare TiO$_2$

Kaewkam et al. [57] studied the UV-assisted TiO$_2$ photocatalytic degradation of virgin LDPE films, investigating the effect of UV-A (longest wavelengths = 352 nm), UV-C (shortest wavelengths = 254 nm), and TiO$_2$. The combination of UV radiation and TiO$_2$ photocatalysis was found to significantly enhance the degradation of virgin LDPE films compared to degradation under UV radiation alone or TiO$_2$ photocatalysis alone. TiO$_2$ fired at 450 °C (anatase + rutile) was photo-catalytically more active than TiO$_2$ (rutile-900 °C) when exposed to UV-A. The UV-assisted TiO$_2$ photocatalysis showed the highest degradation efficiency among the tested conditions. It was also found that TiO$_2$ (rutile) excited by UV-C was more suitable for the photodegradation of LDPE than TiO$_2$ (anatase + rutile) excited by UV-C. The photodegradation of LPDE, in the absence of TiO$_2$, was also studied by exposing the LDPE films to UV-A and UV-C radiations for 3, 5, 7, and 9 days. UV-C radiation resulted in faster degradation of LDPE films compared to UV-A radiation due to its higher energy, which facilitated the breakage of C-H bonds in LDPE. The ambient temperatures of the UV-A and UV-C systems were within the ranges of 30.3–32.7 °C and 36.5–38.6 °C, respectively. The increase in temperature caused by UV light irradiation was considered to have a minimal effect on the degradation of LDPE films.

Nabi et al. [63] studied the photocatalytic degradation of MPs (PS and PE) using TiO$_2$ films under UV irradiation, and the influence of PS sphere size and catalyst preparation was evaluated. The authors prepared three types of TiO$_2$ films (from TiO$_2$ P25) with different physicochemical properties by varying the synthesis solvent: water (WT), ethanol (ET), and Triton X-100 (TXT).

The catalytic performance of the three prepared TiO$_2$ films in the degradation of PS-MPs was evaluated under 12 h of UV light radiation at 254 nm. Degradation percentages of 98.4%, 91.04%, and 69.25% were obtained for the TXT, ET, and WT films, respectively. The same study was conducted only on fluorinated-tin oxide (FTO) (direct photolysis, without a catalyst), resulting in an 8.01% degradation. The superior performance of TXT-TiO$_2$ can be attributed to its lower band energy and efficient charge separation, which were further investigated in detail. As a result, TXT generates a higher number of electron-hole pairs under light irradiation and prolongs the charge separation, leading to significant photoactivity in PS removal. On the other hand, the underwhelming performance of the WT film is likely due to its larger particle size, lower surface area, and limited charge separation ability. The enhanced activity of the TXT film can also be attributed to its

surface hydrophilicity and film texture. Surface hydrophilicity promotes the interaction between semiconductors and plastic, particles that improve the film texture, leading to charge transfer and separation that results in the fast degradation of microplastics.

The catalytic performance of the TXT-TiO$_2$ catalyst was evaluated by varying the size of PS-MP particles, with sizes of 700, 1000, and 5000 nm. Degradation efficiency values of 93.49%, 95.30%, and 99% were obtained, respectively, under 24 h of UV light radiation at 254 nm. This catalyst was also tested in the degradation of PE-MPs, achieving 100% efficiency after 36 h of UV light radiation at 354 nm.

It is important to highlight that the results obtained by Nabi et al. [63], as shown in Table 2, were conducted in the solid phase under ambient air conditions, where a solution of PS spheres (20 μL) was deposited onto the catalyst film as well as onto the clean FTO (without catalyst) and dried at room temperature.

The degradation assay was also carried out in the liquid phase, where 0.05 g of the TXT-TiO$_2$ catalyst was added to a 100 mL solution of PS. A solution of 100 μL of PS (5 μm size) in 100 mL of deionized water was prepared. The solution was continuously stirred during the degradation reaction under 254 nm UV light irradiation, and samples were taken at regular time intervals. The film fabrication process does not involve the use of costly, toxic, or hazardous chemicals, making it highly efficient, beneficial, and economically important. Furthermore, the solid phase photodegradation of microplastics eliminates the release of potentially toxic intermediates into water, unlike liquid phase technologies. Overall, this study presents a green and sustainable method for degrading MP waste in the environment.

Fadli et al. [64] studied the degradation of PE-MPs using TiO$_2$ (P25) catalysts. The degradation test was done by adding PE-MPs scrub-sized 100–150 into distilled water. For the test, 100 mL of distilled water and 50 mg of microplastics were added to a beaker glass, and then 50 mg of catalysts were added to the solution. The solution was stirred continuously during the degradation test. The tests were carried out at room temperature with the help of UV irradiation. Tests were conducted for 1, 2, 3, and 4 h with the same initial amount of MP pollutant. The degradation efficiency increased over time, reaching 56% after 4 h of reaction. The same test was conducted in the absence of a catalyst (direct photolysis), resulting in 100% recovery of the microplastics (0% degradation).

3.2. Modified TiO$_2$

Fadli et al. [64] also studied the catalytic performance of 3%Ag-TiO$_2$ and 3%Ag-TiO$_2$-1%RGO (reduced graphene oxide) catalysts in the degradation of PE. After 4 h of analysis, the degradation efficiency was 68, and 76%, respectively. The improvement in performance compared to that obtained with bare TiO$_2$ could be associated with the high electron mobility properties of silver metal and RGO, which act as efficient electron acceptors and increase induced photon transfer, thereby inhibiting the rate of electron-hole recombination. Additionally, silver metal exhibits strong absorption of UV and visible light, and its higher absorbance of visible light enhances the electron-hole charge separation of the photocatalyst. This results in the creation of more active sites on the catalyst's surface. Furthermore, RGO possesses a large theoretical specific surface area, which enhances electron mobility to RGO and allows for electron storage on its surface. The large surface area also improves the catalyst's adsorption capacity, facilitating contact between the catalyst and the pollutant.

Maulana et al. [65] synthesized Ag/TiO$_2$ nano-composites using the Photo Assisted Deposition (PAD) method. The objective of their research was to investigate the capability of these nano-composites to degrade PE-MPs present in water, specifically by examining the impact of varying particle sizes of microplastics as pollutants in drinking water. The PE-MPs degradation test was performed using the mass loss method. The effectiveness of catalysts in microplastic degradation can be determined by measuring the reduction in microplastic mass before and after subjecting them to a 2 h UV irradiation treatment. The MP particles used varied in size, specifically ranging from 100–125, 125–150, and 150–250 μm, with an initial concentration of 100 ppm. During the degradation process, magnetic stirrers were

employed at a rotational speed of 2000 rpm, along with UV lamp irradiation. The addition of the Ag dopant had a positive impact on microplastic degradation, resulting in a 100% degradation rate within 120 min of irradiation. Among the different particle sizes, the best percentage of degradation was achieved with the 125–150 micrometer size, where 100% degradation was attained after 90 min of irradiation.

Zhou et al. [66] studied the potential of utilizing a TiO$_2$ catalyst in a photocatalytic degradation process to demonstrate the feasibility of MPs. The assays were carried out in a three-electrode quartz cell, and a 0.5 M Na$_2$SO$_4$ electrolyte solution was used. An Ag/AgCl electrode served as the reference electrode, and a Pt wire was employed as the counter electrode. N-TiO2 and Pt/N-TiO$_2$-1.5% were utilized as the photoanodes. The photoanode was prepared through a physical coating process. 5 mg of photocatalyst was dispersed using ultrasound in a mixture consisting of 20 μL of 1-naphthol and 500 mL of ethanol. This mixture was evenly coated onto the FTO glass substrate and subsequently dried at 60 °C for 24 h. They achieved a 29% degradation efficiency. The result showed that inducing an initial rough appearance by hydrothermal treatment was a positive factor affecting the photocatalytic degradation of PET.

Therefore, the performance of TiO$_2$ and modified TiO$_2$ photocatalysts for microplastic oxidation is influenced by various parameters. These include the type of photocatalyst material, dosage of photocatalyst, microplastic concentration, light source and intensity, particle size and morphology, and surface modifications. The choice of photocatalyst material, such as TiO$_2$ or modified TiO$_2$, affects its activity and stability. Particle size and morphology affect the active surface area and mass transfer. Surface modifications, like doping or coatings, can improve the photocatalyst's absorption properties and introduce catalytic sites, enhancing oxidation efficiency.

Regarding ZnO-based and other photocatalytsts, Table 3 summarizes selected results of the photocatalytic removal of MPs by bare and modified ZnO and other systems.

Table 3. Selected results of the photocatalytic removal of MPs by bare and modified ZnO and other photocatalysts.

Photocatalysts	MPs	Conditions		Degradation Efficiency (%)		Ref.
ZnO	ZnO	LDPE	- 6.5 cm^2	- 0.71/0.51 *		[67]
			- 22 cm^2	- 1.17/0.9 *		
		- Particle size: - 1 × 1 cm, - Visible light irradiation, 175 h	- 49 cm^2	- 1.38/1.12 *		
			- 55 cm^2	- 1.51/1.3 *		
	ZnO and MPs extracted from sunscreen	- Simulated sunlight, 12 h - ZnO and MPs extracted from sunscreen		- ZnO enhances 2.5 times the CI *		[68]
	PP	- Particle size: 25 mm^2, [ZnO] = 1 g/L - 6 h, UV-C irradiation, 50 °C,		- >7 ^{WL}		[69]
	GO-ZnO	- [GO-ZnO] = 1500 ppm - pH = 9.88, 30 °C, 2 h		- 39.47 ^{WL}		[61]
	Pt-ZnO	LDPE	- Control (LDPE)	- 0.71/0.51 *		[70]
		- Vis Light irradiation, - 175 h	- ZnO + LDPE	- 1.38/1.12 *		
			- ZnO-Pt + LDPE	- 1.49/1.35 *		

Table 3. *Cont.*

Photocatalysts	MPs	Conditions		Degradation Efficiency (%)	Ref.
Other	PE		- BiOCl	- 0.22 ^{WL}	
			- BiOCl-1	- 5.38 ^{WL}	
	Different types, colors, and sizes of MPs	- Vis. light, 5 h - 1 g/L photocatalyst - Spheres of PE	- BiOCl-1 - pH effect	- MPs are more easily degraded in acidic conditions	[71]
BiOCl			- BiOCl-1 - Color and size effect	- Lower Size→ faster degradation - Light color→ reduce the degradation	
BiOI-Fe$_3$O$_4$	PSL	- Vis light, 24 h - Particle size 1.1 μm (0.05 g/L) H$_2$O$_2$ (0.1 wt.%) - Buffer pH 7	- Absence of photocatalyst	- ≈1 ^{WL}	[72]
			- BiOI	- 38 ^{WL}	
			- Fe$_3$O$_4$	- 12 ^{WL}	
			- BiOI-Fe$_3$O$_4$	- 56 ^{WL}	
Au NPs	LDPE	- Solar irradiation - 240 h, - 1.0 wt.% Au/LDPE		- 90.8 ^{WL}	[73]

* CI/VI values. (Carbonyl index/vinyl index); ^{WL}: degradation efficiency estimated by weight losing.

3.3. Bare ZnO

Tofa et al. [67] tested the degradation of fragmented, low-density polyethylene (LDPE) MP residues by visible light-induced heterogeneous photocatalysis activated by ZnO nanorods (NRs). In an experimental setup, photocatalytic degradation of a 1 cm × 1 cm LDPE film was conducted for a duration of 175 h. The experiment took place in a petri dish containing deionized water and the photocatalyst. Visible light illumination was provided using a 50 W dichroic halogen lamp in an ambient air environment. The photocatalytic oxidation of LDPE resulted in the generation of low molecular weight compounds, including hydroperoxides, peroxides, carbonyl groups, and unsaturated groups. This led to an increase in the brittleness of the LDPE material, accompanied by the formation of wrinkles, cracks, and cavities on its surface. Additionally, it was observed that the surface area of the catalyst played a significant role in enhancing the degradation of LDPE in this work. The evolution of carbonyl and vinyl groups are used as indicators for monitoring the degree of degradation of a polymer. Three catalysts with different surface areas were tested, and carbonyl and vinyl indices (CI and VI) showed that the photocatalytic performance improved with the catalyst surface area.

The relationship between the carbonyl index (CI) and vinyl index (VI) with microplastics degradation can provide insights into the extent and progress of the degradation process. Both CI and VI are indicators of chemical changes occurring during degradation and can be used to assess the degradation level of microplastics. The carbonyl index (CI) is a measure of the carbonyl functional groups formed during degradation. These functional groups, such as aldehydes and ketones, are typically generated due to oxidation reactions. The increase in CI value indicates a higher concentration of carbonyl groups, suggesting a higher degree of degradation. On the other hand, the vinyl index (VI) reflects the degree of unsaturation within the microplastic polymer chain. As degradation occurs, the polymer chain undergoes cleavage and breaks into smaller fragments. This process can lead to the formation of unsaturated bonds, resulting in an increase in the VI value.

Based on the findings of this study, a degradation pathway for LDPE film was proposed. The process begins with the generation of hydroxyl and superoxide radicals from the catalyst. These radicals initiate degradation at vulnerable points in the long polymeric chains, such as chromophore groups and defects. This leads to the formation of low molecular weight polyethylene alkyl radicals, followed by chain breaking, branching, crosslinking, and oxidation of LDPE. Subsequently, peroxy radicals are formed as oxygen is incorporated into the system. These radicals then abstract hydrogen atoms from the polymeric chains, resulting in the formation of hydroperoxide groups. The hydroperoxide groups are significant oxygenated products that govern the rate of photocatalytic degradation. Their dissociation produces alkoxy radicals, which undergo further reactions to generate species containing carbonyl and vinyl groups. These groups contribute to chain cleavage.

The presence of carbonyl and vinyl groups confirms the photo-oxidative degradation of LDPE films in the presence of catalysts. The degradation process ultimately leads to the generation of volatile organic compounds, such as ethane and formaldehyde.

Sun et al. [68] studied the degradation of MPs using ZnO nanoparticle NPs as photocatalysts. Both MPs and ZnO NPs were extracted from a commercial sunscreen. They found that a short exposure duration of 12 h under simulated sunlight did not lead to surface oxidation of MPs. However, when ZnO nanoparticles (NPs) were added, surface oxidation of regular microplastics (MPs) was observed. The presence of ZnO NPs and water did not significantly induce surface oxidation. However, when sunlight was involved, a time-dependent increase in oxidation was observed. With the presence of sunlight, water, and ZnO NPs, the authors demonstrated the photooxidation of MPs by the produced hydroxyl radicals, which promoted the fragmentation of MPs. Spherical MPs were fragmented into smaller pieces with sharper edges, suggesting that primary MPs were transformed into secondary MPs, which were more likely to present on human skin.

This study provides significant insights into the impact of secondary microplastics (MPs) on human health, specifically focusing on the activation of MPs by zinc oxide nanoparticles (ZnO NPs) derived from commercial products. The findings of this research demonstrate the critical importance of understanding the cytotoxicity caused by secondary MPs. These findings underscore the detrimental effects of secondary MPs on cellular function and highlight their potential to induce oxidative stress and mitochondrial dysfunction. By exploring the activation of MPs by ZnO NPs and elucidating their impact on human health, this study fills a crucial knowledge gap in the field. It provides compelling evidence that secondary MPs can trigger adverse effects and pose significant risks to human well-being.

Razali et al. [69] studied the impact of the UV-assisted thermo-photocatalytic reaction on the degradation of polypropylene (PP) macro- and microplastics in a water-based environment over a period of 6 h. Zinc oxide (ZnO) nanoparticles, with a size below 50 nm, were utilized as the photocatalyst in the experiment. The degradation rate of both macro and microplastics made of polypropylene (PP) suspended in water has been significantly influenced by the UV-assisted thermo-photocatalytic reaction using zinc oxide (ZnO) as the catalyst.

Under the influence of UV light, ZnO photocatalyst generates reactive radical species, such as superoxides or hydroxyl radicals, which are highly oxidizing. These radicals swiftly attack and oxidize the polar functional groups present in PP, leading to its degradation. The rate of photodegradation of PP is further enhanced by increasing the reaction temperature, particularly at around 50 °C. This temperature elevation promotes the fragmentation of both macro and microplastics.

Statistical analysis confirmed that the reaction temperature and size of the PP plastic, as well as the interaction between these variables, are important factors to consider. However, the dosage of ZnO catalyst had minimal impact on the degradation of PP plastic.

3.4. Modified ZnO

Tan et al. [61] studied the applicability of photocatalysis in degrading LDPE microplastics by using graphene oxide/zinc oxide (GO-ZnO) photocatalysts under UV light irradiation. In this study, the interaction between pH, temperature, and catalyst loading on the mass loss of LDPE was investigated. Optimal conditions for microplastic mass loss (39.28%) were determined at a pH of 9.81, a temperature of 30 °C, and a catalyst loading of 1500 ppm. Additionally, this study highlighted the applicability of response surface methodology in evaluating the impact of different variables on microplastic mass loss and determining the optimized conditions. According to the Pareto Analysis, the catalyst dosage was identified as the most influential parameter affecting the overall mass loss of microplastics.

Tofa et al. [70] studied the degradation of fragmented microplastics particularly low-density polyethylene (LDPE) film in water, through visible light-induced plasmonic photocatalysts comprising of platinum nanoparticles deposited on zinc oxide (ZnO) nanorods (ZnO-Pt). The introduction of plasmonic metal in modified ZnO-Pt catalysts resulted in approximately a 13% increase in the oxidation potential of LDPE film compared to the ZnO nanorods in their original state. This suggests that incorporating plasmonic metal into ZnO could offer a promising approach to accelerate the oxidation of microplastic pollutants in water using sunlight. Authors found that the incorporation of platinum nanoparticles in the catalyst leads to an improvement in the absorption of visible light, thanks to the plasmon absorption phenomenon. Furthermore, the diffusion of photogenerated electrons from the ZnO nanorod interfaces into the platinum nanoparticles helps to minimize electron-hole recombination. The presence of platinum nanoparticles on ZnO nanorods clearly enhances the efficiency of photodegradation. The carbonyl index and vinyl index experienced a notable increase of 13% and 15%, respectively. These findings strongly indicate that the degradation efficiency of ZnO-Pt plasmonic photocatalysts is significantly improved compared to unmodified ZnO nanorods.

3.5. Other Photocatalysts

The utilization of photocatalysts beyond TiO_2 and ZnO has emerged as a promising alternative for the removal of microplastics present in water. Materials such as graphene, tungsten oxide (WO_3), and molybdenum dioxide (MoO_2) have been investigated for photocatalytic degradation of microplastics. These alternative photocatalysts offer distinct properties and characteristics that can enhance the removal efficiency of microplastics compared to traditional ones. Furthermore, the combination of different photocatalysts in hybrid systems has shown promising potential in efficiently degrading microplastics. These advancements open up new possibilities in the development of photocatalytic technologies to address the issue of microplastics in water.

Jian et al. [71] employed an ultrathin BiOCl (BiOCl-X) material with a high hydroxy content, prepared under room temperature conditions for the photocatalytic degradation of MPs. X represents the load of mannitol added. The researchers investigated its effectiveness in the photocatalytic degradation of microplastics (MPs). Remarkably, BiOCl-X exhibited significant potential for degrading MPs through photocatalysis, surpassing the performance of BiOCl nanosheets. The mass loss of plastics achieved using BiOCl-X was found to be 24 times greater compared to the degradation achieved with BiOCl nanosheets. Furthermore, the study revealed that smaller microplastics degraded faster, while light-colored or stable microplastics experienced a significant reduction in photocatalytic degradation. Additionally, the degradation of microplastics was found to be more pronounced in acidic conditions, whereas the Coulomb repulsion in alkaline solutions protected them from degradation.

Khairudin et al. [72] proposed a promising method of degrading the 1.1 μm polystyrene latex (PSL) beads MPs using a self-propelled and magnetically recovered $BiOI-Fe_3O_4$ microswimmer. The findings demonstrate the effective degradation of 64% of polystyrene MPs within 120 h using flake-like $BiOI-Fe_3O_4$ microswimmers. These microswimmers

significantly reduce the concentration of MPs in an aqueous solution from 0.05 g/L to 0.018 g/L. The movement of the microswimmers is induced by the presence of visible light and H_2O_2 fuel, which decomposes into oxygen bubbles. Observations reveal that the microswimmers, with an average particle size of 3.913 µm, can achieve a reasonable speed of 3.0498 µm/s under 3.6 W visible light irradiation and a 5 wt% H_2O_2 concentration. Moreover, it is evident that PSL-MPs degrade rapidly when exposed to visible light for less than 24 h. The degradation of PSL through photocatalytic processes was investigated under visible light irradiation for 24 h, comparing the absence of a photocatalyst with the presence of pristine Fe_3O_4, pristine BiOI, and a composite BiOI-Fe_3O_4 microswimmer. There was no significant degradation of PSL (~1%) in the absence of a photocatalyst after 24 h of light exposure. In the presence of mesoporous Fe_3O_4 with a high surface area of 63.0857 m^2/g, a 12% degradation of PSL was observed. The low percentage removal of PSL can be attributed to the high band gap energy (3.2 eV) of the synthesized Fe_3O_4, requiring more photon energy to facilitate electron transfer from the valence band to the conduction band, resulting in reduced degradation performance. However, when the composite BiOI-Fe_3O_4 microswimmer was present, a 56% degradation of PSL was achieved under visible light irradiation, surpassing the performance of the pristine BiOI microswimmer, which achieved 38 degradation under the same illumination period of 24 h. The improved degradation performance of the composite microswimmer can be attributed to the mesoporous structure, which slightly increases the specific surface area and the number of surface-active sites.

Olajire et al. [73] studied the photocatalytic potential of Au NPs through the solid-phase degradation of low-density polyethylene (LDPE) film. The photoinduced degradation of LDPE@Au nanocomposite film was higher than that of the pure LDPE film. The weight loss of LDPE@Au (1.0 wt%) nanocomposite film steadily increased and reached 51.4% in 240 h under solar light irradiation, compared to the photo-induced LDPE with only 8.6 ± 0.7%. However, LDPE film with 1.0% Au NPs gave a weight loss value of 4.72 ± 0.71 under the dark condition at the end of 240 h. Thus, LDPE film with 1.0% Au NPs showed a degradation efficiency of 90.8% under solar irradiation after 240 h. The reusability of the nanoparticles in the photocatalytic degradation reaction up to five consecutive cycles without substantial loss in its catalytic performance confirmed the sustainability of the system.

It is important to highlight that the efficiency of removing microplastics from water is influenced by the functional groups present in the materials used. For example, the polarity of microplastics and organosilanes has been found to have a strong effect on removal efficiency [74]. The alkyl group in alkyltrichlorosilanes also plays a major role in the agglomeration and fixation of microplastics, with intermediate chain lengths between 3 and 5 carbon atoms being the most suitable [75]. Various factors, such as coagulant type and dose, microplastic material, shape, and size, as well as water quality, can also impact the removal efficiency of microplastics in drinking water treatment processes [76]. The combination of separation and degradation processes has shown promising results in achieving high removal efficiency for microplastics and nanoplastics in water [77]. Additionally, optimizing treatment conditions and exploring emerging technologies such as sol-gel technology can further enhance the removal efficiency of microplastics in water treatment [78].

In conclusion, these studies provide valuable insights into the photocatalytic degradation of microplastics using various photocatalysts. The investigations shed light on the degradation mechanisms, optimization of reaction conditions, and potential impacts on human health. The findings contribute to the development of photocatalytic technologies to mitigate the environmental impact of microplastics in water systems. However, further research is needed to explore the long-term performance, scalability, and real-world applicability of these photocatalysts for effective microplastic removal. In this regard, considering the results presented in this section and other unreported studies, it can be said that the photocatalytic degradation efficiency of MPs (Microplastics) present in water is mainly

affected by factors stemming not only from the photocatalyst but also from the properties of the MP itself and the reaction conditions in which it takes place. Figure 2 summarizes the main factors that affect the efficiency of MP photodegradation in water.
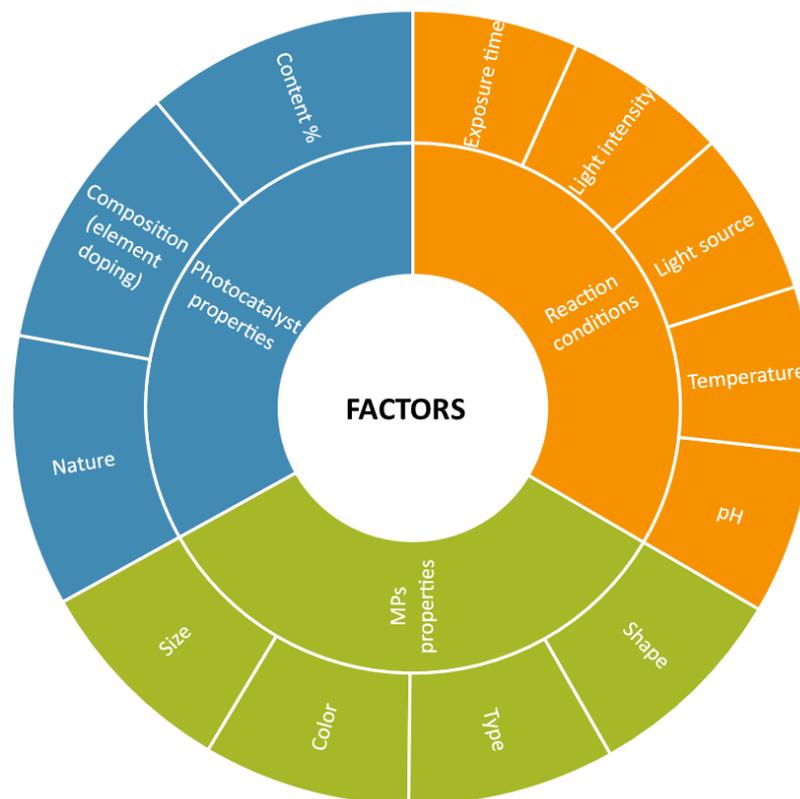

Figure 2. Factors affecting the photocatalytic degradation efficiency of MPs in water.

4. Conclusions

The issue of MP pollution has garnered significant attention due to its detrimental impact on the environment. However, the search for effective methods to address the remediation of MPs remains a substantial challenge. This comprehensive review examines the current photocatalysts used for MP degradation and explores the factors affecting the degradation efficiency.

The photocatalytic degradation efficiency of MPs present in water is mainly affected by factors stemming not only from the photocatalyst but also from the properties of the MP itself and the reaction conditions in which it takes place.

The review highlights the advantages and disadvantages of the different methods reported for the removal of MPs from water. Therefore, the selection of appropriate decomposition methods for MP treatment, considering the different types of MPs, holds significant importance. This review enhances our understanding of MP decomposition through the photocatalytic process and provides valuable insights for improving the decomposition performance of MPs.

Conflicts of Interest: The authors declare no conflict of interest.

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